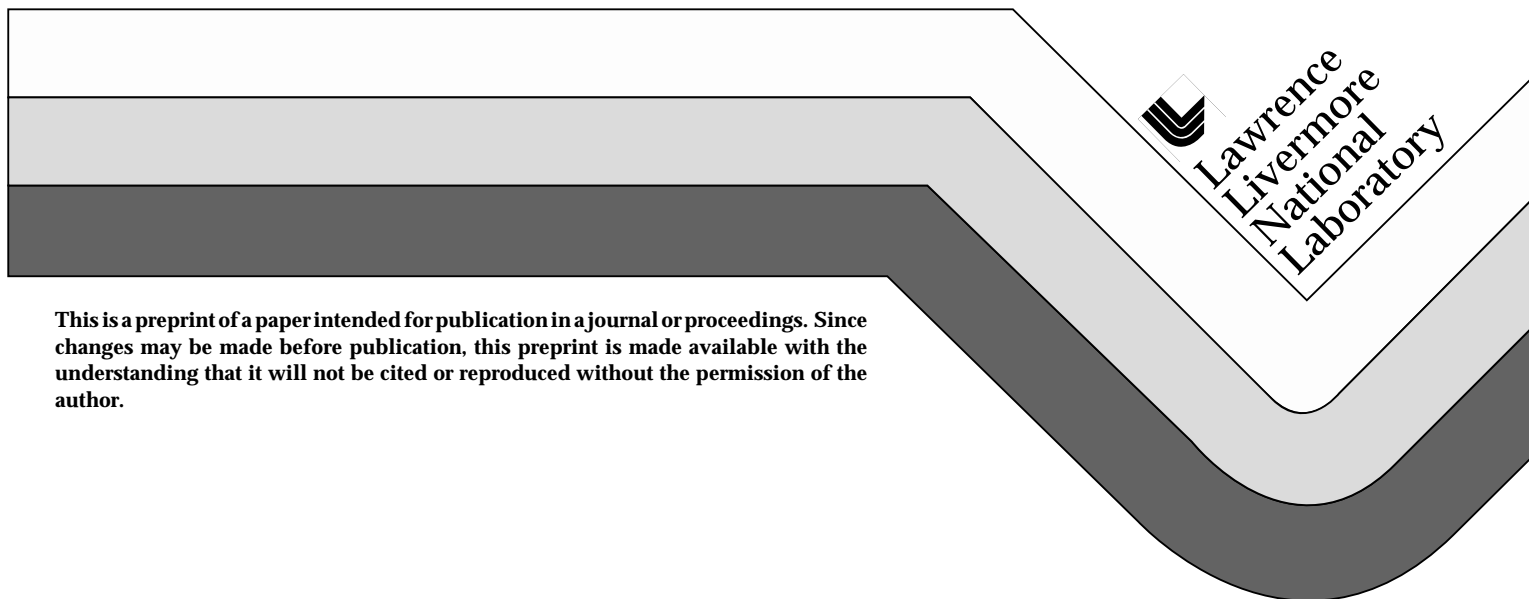


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CARBONACEOUS MATERIALS AS LITHIUM INTERCALATION ANODES

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ABSTRACT

Commercial and polymer-derived carbonaceous materials were examined as lithium intercalation anodes in propylene carbonate (pyrolysis < 1350°C, carbons) and ethylene carbonate/dimethyl carbonate (graphites) electrolytes. The reversible capacity (180-355 mAh/g) and the irreversible capacity loss (15-200% based on reversible capacity) depend on the type of binder, carbon type, morphology, and phosphorus doping concentration. A carbon-based binder was chosen for electrode fabrication, producing mechanically and chemically stable electrodes and reproducible results. Several types of graphites had capacity approaching LiC_6 . Petroleum fuel green cokes doped with phosphorous gave more than a 20% increase in capacity compared to undoped samples. Electrochemical characteristics are related to SEM, TEM, XRD and BET measurements.

INTRODUCTION

Carbon is an attractive candidate for use in Li-intercalation negative electrodes for lithium-ion or rocking-chair rechargeable cells because of its low cost, chemical stability, and excellent reversibility for Li insertion. Cells containing Li-intercalated carbon electrodes are more easily fabricated than similar cells containing lithium metal because the electrode components are stable in air. A variety of carbonaceous materials (graphite, petroleum coke, carbon black, carbon fiber, glassy carbon, etc.), having a wide spectrum of physical and chemical characteristics, has been evaluated in Li-intercalation electrodes (1-3). However, the factors which influence the electrode capacity, irreversible capacity loss, voltage profile and cycle life are not fully understood. The variety of commercial carbonaceous materials with different particle morphologies and structures, varying composition of carbon and other elements, and different surface properties, makes analysis and correlation of the electrochemical results particularly difficult. On the other hand, the availability and low cost of these materials make them particularly attractive.

The purpose of this work is to evaluate the suitability of both commercial and polymer-derived carbons. The major effort is directed at developing an understanding of the relationship between carbonaceous materials physicochemical properties and their electrochemical performance. In addition, a goal of this investigation is to identify low-cost, commercially available carbons which may be suitable in Li-ion cells.

EXPERIMENTAL

The materials that were investigated in this study are listed in Tables 1 and 2, along with some physical data obtained from the manufacturer or measured in our laboratories. The carbons and graphites obtained from different commercial sources (Lonza G+T Ltd., Repsol Petrolleo, Superior Graphite Co., Cabot Corp., Asbury Graphite Mills, Inc.) are divided into two classes (graphitized or non-graphitized) based on the information provided from the manufacturers and/or their pyrolysis temperature ($T_p < 1350^\circ\text{C}$ considered non-graphitized). This distinction was made because a different electrolyte was used to evaluate the graphitized and non-graphitized carbon (see below). For this study, the carbonaceous materials obtained from Lonza G+T Ltd. and Superior Graphite Co. are considered graphitized. In addition to the carbons that were obtained from outside sources, several polymer-based carbons were also synthesized in our laboratory for evaluation. These materials were obtained by carbonizing polyacrylonitrile (PAN, DuPont), phenolic resin (Reichhold Chemical) and polyfurfuryl alcohol at 1050°C for 3 hr in a

nitrogen atmosphere. Polyfurfuryl alcohol was obtained from the phosphoric acid-catalyzed polymerization of furfuryl alcohol (QO Chemicals). The carbonized materials were ground and sieved to between 30-60 μm before testing in an electrode structure.

Omaru and co-workers (4, 5) have observed that the presence of phosphorus in the carbonaceous materials enhances its capacity for Li intercalation. In their experiments, phosphorus was added to polyfurfuryl alcohol, and the mixture was then heated to 1200°C to form the phosphorous-doped carbon. We have also investigated the influence of a phosphorus additive on the ability of carbon to intercalate Li. Our experiments differ from those of Omaru and co-workers in that the phosphorus was added as H_3PO_4 to a petroleum coke. A slurry of petroleum coke powder and a known amount of 10 wt% concentrated H_3PO_4 in acetone solution was air dried at room temperature and then heat treated at 1050°C for 3 hours to form the phosphorus-doped carbon. Elemental analysis for phosphorus content was performed by Galbraith Laboratories.

The powder materials with known particle size were used (as-received from the manufacturer) directly in the electrode fabrication procedure. The large granular or bead forms are first ground using a mortar and pestle and then sieved to between 30 and 60 μm . The electrodes were prepared using a commercial carbon fiber sheet (Lydall Corp., 0.12 mm thick) as the support matrix, and either PTFE (8%), PVDF (6%) or a polymer-derived carbon (10-15%) as binder. A slurry containing the carbon particles, binder and acetone was spread onto the carbon fiber support and allowed to dry. In experiments with PVDF and PTFE binders, the composite was then hot pressed at 1000 psi. The PVDF-bonded electrodes were dried in a vacuum oven at 110°C for 1 hr, followed by heat treatment in vacuum at 170°C for another 1 hr. The PTFE-bonded electrodes were vacuum dried at 110°C for 1 hr, followed by heat treatment in air at 350°C for 30 minutes. Electrodes with the polymer-derived carbon-based binder were pyrolyzed at 1050°C (in N_2) directly without compression creating a composite carbon electrode. The final electrode thickness was between 0.26 and 0.30 mm.

The non-graphitized carbons were tested in propylene carbonate (Grant Chemical)-based electrolytes with a 9:1 mixture of 0.5 M lithium trifluoromethanesulfonimide ($\text{LiN}(\text{CF}_3\text{SO}_2)_2$, tradename HQ115, 3M Corp) and 0.5 M LiAsF_6 (FMC Corp). The graphitized materials were studied in 0.5 M HQ115/(50/50) ethylene carbonate/dimethyl carbonate (Grant Chemical). Different solvents were used with the nongraphitized and graphitized carbons to minimize the irreversible capacity loss.

The electrochemical experiments were carried out in a 15 ml, three-electrode cylindrical cell in which the electrodes and separator are placed horizontally and stacked vertically. The geometric surface area of the working electrode is 1.12 cm^2 . A composite of lithiated carbon

paper and lithium foil (Cyprus Foote Mineral) was used as the counter electrode and lithium foil was used as the reference electrode. Whatman fiberglass filters (934-AH) was used as the separator between the working and counter electrodes. The cells were constructed and tested at $16 \pm 2^\circ\text{C}$ in a dry argon-atmosphere glove box (< 10 ppm water). The charge/discharge rate that was used is generally C/24 based on the composition LiC_6 . Electrochemical studies were performed using a 64-channel Maccor battery tester.

High Resolution Transmission Electron Microscopy (HRTEM) using a JEM-200CX and TOPCON-002B operated at 200 kV was used to analyze the crystallographic structure and particle morphology of the carbonaceous materials. Samples for the HRTEM studies were ground to fine powders in acetone and a drop of the suspension was placed onto 3-mm copper grids supporting a holey carbon film for examination. The x-ray diffraction (XRD) analyses were performed using a diffractometer (Siemens Diffractometer OSP, Model:D500, Germany). The samples were first ground to a fine powder, and then placed on a double-sided tape that was stuck to a glass slide which served as the specimen holder. Step-scanned intensity data were generated using $\text{CuK}\alpha$ radiation at a voltage of 40 kV and current of 30 mA. The data were gathered at room temperature over a 2θ range from 20° to 60° and 2-s count time at each step. SEM observations were performed using a Hitachi S570 Scanning Electron Microscope.

RESULTS AND DISCUSSION

Effect of Binder.

Studies by Tamura et al. (6) indicate that the choice of binder can have a major influence on the electrochemical performance of carbon for Li intercalation. Their findings showed that polyethylene was a better binder than polystyrene. Preliminary experiments at our laboratories indicated that both the irreversible capacity loss on the first cycle and the reversible capacity for lithium intercalation were dependent on the type of binder used in the carbon electrode. The experimental results obtained with a graphite powder (Lonza SFG6 graphite) using different binders are compared in Table 3. The highest capacity (expressed here in terms of x in Li_xC_6) and the lowest first-cycle capacity loss were obtained with the electrode prepared from the polymer-derived carbon binder. This type of electrode also shows excellent mechanical and chemical integrity in the electrolytes. The results with other graphites show a similar trend with choice of binder. Because of these results and the robustness of the use of the carbon binder, this type of electrode fabrication was used exclusively in subsequent experiments. Performance data for these electrodes (capacity, capacity loss) are from the first-cycle results and are expressed in

terms of the total weight of the composite carbon electrodes (i.e., studied carbon, 6% paper and 12% binder). The capacity and capacity loss for the Lydall paper are about 280 and 135 mAh/g, respectively. Those for carbon binder are calculated to be 280 mAh/g (capacity) and 300 mAh/g (capacity loss). Performance of Lydall paper and Lydall paper-carbon binder electrodes in both PC and EC/DMC systems are comparable.

Lithium Intercalation Studies

The physicochemical parameters and performance data for the graphitic materials used in this study are tabulated in Table 1. The Lonza G+T graphites (SFG and KS series) are highly anisotropic synthetic graphites which have been heat treated at temperatures up to 3000°C before grinding and then fractionated to the appropriate particle size range. The TEM and SEM observations show that these graphite particles resembled flat platelets (flat lamellae) with well-defined basal planes. The reversible capacities observed with these materials are about 320-360 mAh/g, which correspond to the x -values given in Table 1. The results further show that the graphite particle size in the range of 6-75 μm and the BET surface areas do not have an effect on their capacity under the experimental conditions selected. Natural-flake and purified-flake graphites from Superior Graphite (SG2933 and BG39, respectively), which have large crystallite size L_c , tend to have a considerably lower capacity than the theoretical value of 372 mAh/g. The particle morphology of the graphite from Superior Graphite was similar to that of the material from Lonza. XRD analyses of these samples indicate a $d(002)$ spacing which is close to the measured value of 0.335 nm for graphite. The graphitized (2700°C) Cabot Sterling R carbon black has a surprisingly low capacity ($x = 0.53$), and high irreversible capacity. The XRD data for this heat treated materials yields $d(002)$ spacing of 0.344 nm while that for the as-received Sterling R samples is about 0.35-0.36 nm. The capacity for this carbon black that was not graphitized, on the other hand, was considerably higher ($x = 0.92$ in EC/DMC based electrolyte); this result is not fully understood at this time. Performance data for the Sterling R sample are comparable in both EC/DMC and PC (Table 2) based electrolytes.

Examples of the electrode potential profiles as a function of Li intercalation capacity, x (Li_xC_6), for electrodes prepared from various types of graphites are presented in Figure 1. Lithium intercalation/deintercalation occurs at potential less than 0.3 V vs. Li/Li^+ , for the highly graphitic materials such as SFG6 and natural flake graphite SG2933. At least three potential plateaus can be observed (SFG6) which are associated with the staging phenomena for intercalation, and are typical of the materials obtained from Lonza G+T.

The physicochemical parameters and performance data for the non-graphitized materials used in this study are tabulated in Table 2. The samples of petroleum coke and carbon black have amorphous carbon structures, and TEM shows only short-range order of the basal planes. Many of the cokes have capacities of about 230 mAh/g. Of the petroleum cokes studied here, the Repsol FGC has the highest capacity. However, it also has the highest capacity loss in the first cycle. The two carbon blacks have a relatively high capacity, but they also show a high irreversible capacity. The charge/discharge profiles for selected petroleum cokes and carbons are shown in Figure 2. The curves for these non-graphitic materials can vary substantially, but are generally noted by their gradual change in potential as a function of lithium capacity.

Electrode materials obtained from the carbonization of a polymer provide a convenient and high-purity carbon source. In this study, electrodes prepared from PAN- and phenolic resin-derived materials showed a capacity of 219 and 182 mAh/g, respectively. On the other hand, the carbon obtained from polyfurfuryl alcohol had a capacity that was substantially higher, 305 mAh/g, which may be attributed to the presence of phosphorus in the sample. Phosphoric acid was used to catalyze the polymerization of furfuryl alcohol, and the phosphorus remains after carbonization.

To date, the highest reversible capacity which is obtained in our studies is 425 mAh/g, which was obtained with phosphorus-doped carbon-foams that were synthesized from the phase separation of polyacrylonitrile/solvent mixtures at Lawrence Livermore National Laboratory (7, 8). Because of these encouraging results, experiments were initiated to investigate the intercalation of Li in phosphorus-doped petroleum coke.

Lithium Intercalation in Phosphorus-Doped Petroleum Coke

Repsol Petrolleo “fuel green coke” was used here to study the effect of phosphorous doping. It is produced from petroleum residues that are carbonized at 480°C. The manufacturers report that this carbonaceous material has a very high content of nitrogen, sulfur and oxygen, but a very low metal content (mainly Ni and V). A more quantitative composition is not available at this time. X-ray diffraction analyses by Jimenez Mateos (9) on similar petroleum cokes from Repsol Petrolleo show the highly turbostratic structure of these green fuel cokes, which is gradually eliminated by heat treatment. The d(002) spacing of the petroleum coke carbonized at 480°C, which was examined by Jimenez Mateos, was 0.344 nm, and heat-treatment temperatures of >1300°C were required before a measurable decrease in the d(002) spacing is observed.

Representative potential-capacity profiles for the intercalation of Li in petroleum coke with and without phosphorus are presented in Figure 3. The curves indicate that the potential for

intercalation, at a given capacity, is higher for the phosphorus-doped carbon, but in general, the potential-capacity profiles are similar. There is evident, however, a slight plateau in the curve for the phosphorus-doped materials during deintercalation at near 0.9 V. A similar plateau was also observed by Omaru et al. (4) with their phosphorus-doped carbon fibers although deintercalation of lithium from these materials occurred at lower potentials (relative to undoped sample).

The phosphorus-doped petroleum coke used in the present study differs in preparation from the phosphorus-doped carbons investigated by Omaru et al. (4,5). These earlier studies included the phosphorus-containing compound in the precursor prior to the formation of the carbonaceous material at elevated temperatures. In the present study, the phosphorus-containing compound was added to the petroleum coke and then heat treated. The net effect may be that the phosphorus species in the earlier studies are incorporated in the bulk structure of the carbonaceous material, while the addition of a phosphorus compound to the petroleum coke in our studies may lead to the deposition of phosphorus on the surface of the carbonaceous materials. However, this has not been experimentally verified.

The variation in the lithium-intercalation capacity of petroleum coke that is doped with different phosphorus concentrations is shown in Figure 4. There is a significant enhancement in the reversible Li capacity with an increase in the phosphorus content to 3.35%, and a trend to a lower capacity loss with an increase in phosphorus doping. Omaru and co-workers (4,5) suggested that phosphorus exists in their samples as a compound of the form $(C_6H_5O)_2P(=O)OH$, which enhances the capacity of the phosphorus-doped carbon for lithium intercalation. No information is available in our studies on the location or species of phosphorus compound that may be present in the petroleum coke. Other studies (10-12) suggest that P-O species are likely to be present after impregnation of carbon with phosphorus compounds and subsequent heat treatment. These species are believed to be bonded to the surface of the carbonaceous material at the edge-plane sites. Oh and Rodriguez (12) suggested that phosphorus is incorporated into the structure at the edge-plane sites of the carbon particle. Because phosphorus has a larger atomic size (0.106 nm versus 0.077 nm) than carbon (12), it is conceivable that the phosphorus atoms at the edge-plane sites may serve to expand the layer planes at the surface of the particles and facilitate intercalation by lithium. The XRD results, which showed no measurable change in the d(002) spacing of the phosphorus-doped petroleum coke, appears to be consistent with this conclusion.

SUMMARY

Polymer-derived carbon binder is preferred over PVDF and PTFE because it produces thin electrodes with good chemical, mechanical and electrochemical properties. Lonza graphites show LiC_6 composition with low irreversible capacity loss. Natural graphites give lower capacity, $x \sim 0.85$. Many types of non-graphitic materials (both commercial and polymer-derived) yield reasonable capacities ($x > 0.6$) but carbon blacks have the largest x values ($x = 0.88$ - 0.93). Phosphorus-doped fuel green coke shows increased capacity over the undoped cokes. It is speculated that the effect of phosphorus is to enhance the intercalation of Li by expanding the layer plane spacing at the edge of the structure.

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Table 1. Physicochemical properties and performance data¹ of graphites

Sample	Source	Type	Part. size ² (μm)	BET area ² (m^2/g)	L_c ² (nm)	d_{002} ² (nm)	x in Li_xC_6	Irr. cap. loss (mAh/g)
SFG6	Lonza	Synthetic grap.	6	15.2	>100	0.336	0.95	70
SFG15	"	"	15	8.8	>120	0.336	0.90	64
SFG44	"	"	44	4.2	<200	0.336	0.93	108
SFG75	"	"	8-96	3.5	>200	0.336	0.95	77
KS6	"	"	6	22	65	0.336	0.85	60
SG2933	Superior	purified flake natural graphite	30-40 ³	-	>2000	0.335	0.86	76
BG39	Superior	battery grade flake natural gra.	7	-	>2000	0.336 ⁴	0.87	98
Sterling R2700	Cabot	C black, heat treated to 2700°C	0.075	30 ⁴	-	0.344 ⁴	0.53	152

1 Electrolyte is 0.5M HQ115 / 50:50 EC:DMC. C/24 rate.

2 Data obtained from respective manufacturer information sheets unless indicated otherwise.

3 Sieved to between indicated range.

4 This study.

Table 2. Physicochemical properties and performance data¹ of various cokes and carbons

Sample	Source	Type	Part. size (μm)	BET area ² (m^2/g)	d_{002} ² (nm)	x in Li_xC_6	Irr. cap. loss (mAh/g)
FGC	Repsol	petroleum fuel green coke	30-60	3.3 ³	0.349 ³	0.69	188
LQNC	Repsol	needle coke	30-60	6.7 ³	0.349	0.63	104
SGC	Repsol	sponge coke	30-60	1.2 ³	-	0.59	90
XP30	Conoco	petroleum coke	30-60	-	0.345 ³	0.59	55
FC250	Lonza	petroleum coke	30-60	-	-	0.62	70
DB40R	Asbury	carbon black	30-40	31	-	0.88	188
Sterling R	Cabot	carbon black	0.075	25 ³	-	0.93	140
PANF	Aldrich ⁴	PAN-derived C	30-60	-	-	0.59	95
RESINF	Reichhold ⁴	RESIN-derived C	30-60	-	-	0.49	82
PFAF	QO Chemicals ⁵	PFA-derived C	30-60	-	-	0.82	116

1. Electrolyte is 10% 0.5M LiAsF₆ / 0.5M HQ115 / PC. C/24 rate.

2. Data obtained from respective manufacturer information sheets unless indicated otherwise.

3. This study

4. Polymer source. Pyrolysis at 1050°C for 3hr to produce carbon materials.

5. Monomer source. Phosphoric acid (5%) catalyzed polymerization. Pyrolysis as in 4.

Table 3. Performance data for SFG6 electrode with different binders

Binder	x in Li_xC_6	Irreversible capacity loss (mAh/g)
PTFE	0.66	150
PVDF	0.79	102
carbon-based	0.95	70

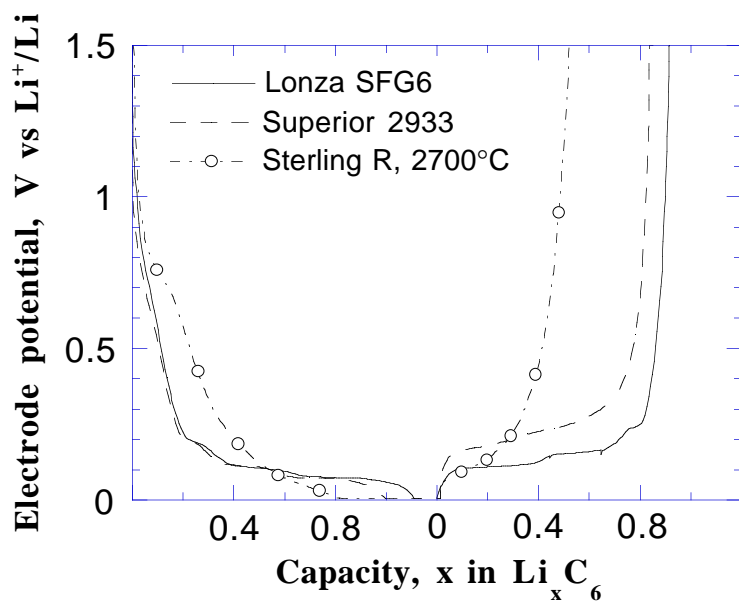


Figure 1. Discharge/charge profiles of several anodes containing graphite and graphitized materials in 0.5M $\text{LiN}(\text{CF}_3\text{SO}_2)_2/(50:50)$ EC:DMC electrolytes. C/24 rate.

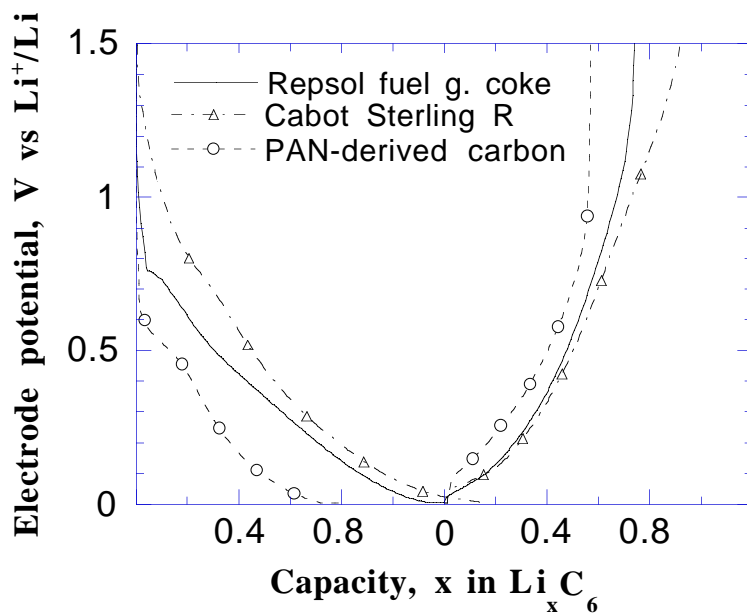


Figure 2. Discharge/charge profiles of anodes containing cokes and carbon materials in 10% 0.5M LiAsF_6/PC in 0.5M $\text{LiN}(\text{CF}_3\text{SO}_2)_2/\text{PC}$ electrolytes. C/24 rate.

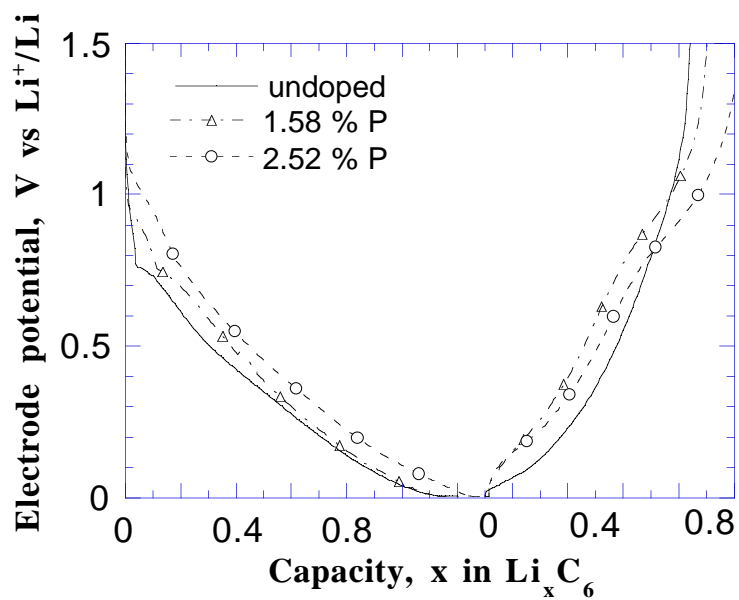


Figure 3. Comparison of discharge/charge profiles of undoped versus P-doped Repsol fuel coke. Electrolyte, 10% 0.5M LiAsF₆/PC in 0.5M LiN(CF₃SO₂)₂/PC. C/24 rate.

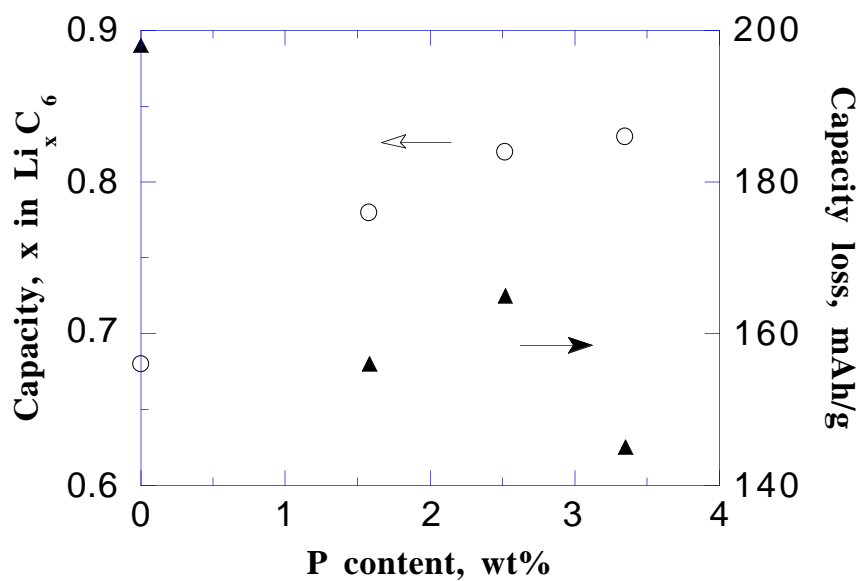


Figure 4. Capacity and irreversible capacity loss as a function of P doping content.

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